Density Functional Theory Characterization of the Multiferroicity in Spin Spiral Chain Cuprates

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(Dated: February 1, 2008)

The ferroelectricity of the spiral magnets $LiCu_2O_2$ and $LiCuVO_4$ was examined by calculating the electric polarizations of their spin spiral states on the basis of density functional theory with spin-orbit coupling. Our work unambiguously reveals that spin-orbit coupling is responsible for the ferroelectricity with the primary contribution from the spin-orbit coupling on the Cu sites, but the asymmetric density distribution responsible for the electric polarization occurs mainly around the O atoms. The electric polarization is calculated to be much greater for the *ab*- than for the *bc*-plane spin spiral. The observed spin-spiral plane is found to be consistent with the observed direction of the electric polarization for $LiCuVO_4$, but inconsistent for $LiCu_2O_2$.

In the past several years there has been a revival of interest in understanding magnetic ferroelectrics because of their potential applications in novel magnetoelectric and magneto-optical devices [1, 2, 3, 4, 5]. In these multiferroics, the paramagnetic phase is centrosymmetric, and electrical polarization appears only at the transition to a magnetically ordered phase, which is responsible for removing the inversion symmetry thereby generating a polar field. Two mechanisms of multiferroicity have been proposed in the literature. The exchange striction due to the symmetric parts of the exchange coupling appears relevant for the multiferroicity in systems such as RMn_2O_5 [6]. The ferroelectricity (FE) in spiral magnets has been suggested to originate from spin-orbit coupling (SOC) [7, 8, 9, 10]. However, this suggestion has never been verified by first principles electronic structure studies.

Very recently, FE was discovered in two cuprates $LiCu_2O_2$ [11] and $LiCuVO_4$ [12]. These oxides contain spin-frustrated CuO_2 ribbon chains that are made up of edge-sharing CuO_4 squares with spin-$\frac{1}{2}$ magnetic ions Cu^{2+}, for which an unpaired spin resides in the e_g orbital (commonly referred to as the $d_{x^2-y^2}$ orbital, but the d_{xy} orbital in the local axis system adopted in the present work). Due to the competition between nearest-neighbor (NN) ferromagnetic and next-nearest-neighbor antiferromagnetic interactions in each CuO_2 chain, a spin spiral state can set in along the chain direction (i.e., the *b* direction) at low temperature [13]. Neutron diffraction studies showed that the Cu^{2+} moments lie in the CuO_2 ribbon plane (i.e., the *ab*-plane) in the spin spiral state of both $LiCu_2O_2$ [14] and $LiCuVO_4$ [15]. Results of a recent ESR study [16] on $LiCu_2O_2$ are consistent with the *ab*-plane spin spiral. Below the temperature of the spiral-magnetic order, the electric polarization is found to be along the *a* direction in $LiCuVO_4$ [12], but along the *c* direction in $LiCu_2O_2$ [11]. This difference in the electric polarization directions is puzzling because, according to the Katsura-Nagaosa-Balatsky (KNB) model [7], the electric polarization along the *a*-direction is asso-

TABLE I: Electric polarizations (in units of $\mu C/m^2$) of $LiCu_2O_2$ and $LiCuVO_4$ calculated for the *ab*-, *ac*-, and *bc*-plane spin spiral states of Fig. 2 using the experimental (EXP) centrosymmetric structures and the optimized (OPT) structures.

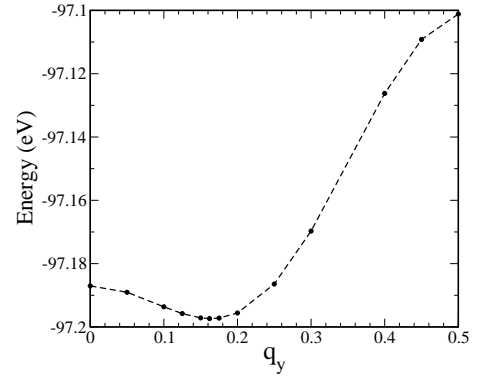|	$\mathbf{P}(ab)$	$\mathbf{P}(ac)$	$\mathbf{P}(bc)$
$LiCu_2O_2$ (EXP)	(51.4,0,0)	(0,0,0)	(0,0,-9.8)
$LiCu_2O_2$ (OPT)	(441.4,0,0)		(0,0,-191.8)
$LiCuVO_4$ (EXP)	(103.5,0,0)	(0,0,0)	(0,0,-15.7)
$LiCu2O4$ (OPT)	(595.6,0,0)		(0,0,-223.0)

FIG. 1: Total energy $E(\mathbf{q})$ calculated for the spin spiral state of $LiCu_2O_2$ as a function of $\mathbf{q} = (0.5, q_y, 0)$ on the basis of the non-collinear LDA+U method using a unit cell containing four formula units.

ciated with the *ab*-plane spin spiral, and that along the *c*-direction with the *bc*-plane spin spiral. However, it is unclear whether the KNB model is applicable to the e_g systems [12] because it was formulated for a t_{2g} system. Furthermore, in their recent study of the spiral magnet $LiCuVO_4$, Jia *et al.* reported [17] that the SOC on the ligand O 2p orbitals plays a more important role than does the SOC on the Cu 3d orbitals. It is important to verify whether or not this conclusion is correct.
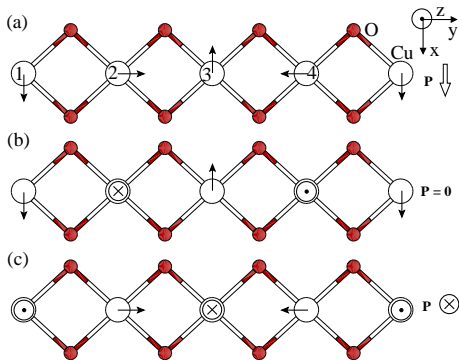
FIG. 2: (color online) Spin arrangements in the (a) *ab*-, (b) *ac*-, and (c) *bc*-plane spin spiral states using the $1 \times 4 \times 1$ supercell. The large white and the small red circles represent the Cu and O atoms, respectively. The legends $\odot$ and $\otimes$ denote z and $-$z directions, respectively. The directions of the electric polarization corresponding to a given spiral plane are also shown. In the present work, the *a*, *b* and *c* axes correspond to the local *x*, *y* and *z* axes, respectively.

In this Letter, we address the aforementioned issues on the basis of non-collinear fully relativistic density functional calculations for $LiCu_2O_2$ and $LiCuVO_4$. The electric polarizations associated with the non-collinear spin-orbit coupled states are calculated using the modern polarization theory [18] for the first time. To the best of our knowledge, this is the first study on multiferroicity in spiral magnets using first principles method with the SOC effect included. Our electronic structure calculations were carried out using the local density approximation (LDA) on the basis of the projector augmented wave method [19] encoded in the Vienna ab initio simulation package (VASP) [20]. The plane-wave cutoff energy was set to 400 eV. To properly describe the strong electron correlation in the 3d transition-metal oxide, the LDA plus on-site repulsion U method (LDA+U) was employed [21]. In the following, we report results obtained with U = 6 eV and J = 0 eV on Cu, but our results with other U values between $4 - 7$ eV are similar.

In the absence of SOC, the incommensurate spiral magnetic order can be simulated without resorting to the supercell technique due to the generalized Bloch theorem [22]. A neutron diffraction study [14] showed that the spin structure of $LiCu_2O_2$ is helimagnetic with propagation vector $\mathbf{q} = (0.5, 0.174, 0)$. We performed a series of calculations [23] for the spin spiral state with propagation vector $\mathbf{q} = (0.5, q_y, 0)$. The dependence of the electronic energy $E(\mathbf{q})$ upon q_y is presented in Fig. 1, which shows that the energy at $q_y = 0$ (i.e., the FM arrangement between all NN's) is lower in energy than that at $q_y = 0.5$ (i.e., the AFM arrangement between all NN's). This is in accord with the FM nature of the NN exchange interaction. The energy minimum occurs at around $q_y = 0.165$, in good agreement with the experimental value of $q_y = 0.174$. This agreement indicates

that the spin spiral ground state of a system with spin frustrated CuO_2 ribbon chains can be predicted by non-collinear LDA+U calculations.

To see if the LDA+U method can describe the FE in $LiCu_2O_2$ as well, we calculated the electric polarization of the spin spiral state with $q_y = 0.174$ using the Berry phase method [18]. This calculation leads to negligible electric polarization. As a possible reason for this failure, we considered the lack of geometry relaxation in the spin spiral ground state. However, LDA+U calculations for the fully optimized structure of $LiCu_2O_2$ does not lead to any appreciable electric polarization. Similarly, our LDA+U calculations for the spin spiral state of $LiCuVO_4$ show no electric polarization. Consequently, the exchange striction is not an appropriate mechanism of electric polarization for $LiCu_2O_2$ and $LiCuVO_4$.

The above observation led us to examine SOC effects on the electric polarization in the spin spiral states of $LiCu_2O_2$ and $LiCuVO_4$. We carry out LDA+U+SOC calculations for the $\mathbf{q} = (0, 0.25, 0)$ spiral states [24] with three different spin spiral arrangements, shown in Fig. 2, by using a $1 \times 4 \times 1$ supercell. Our calculations for $LiCu_2O_2$ give rise to substantial electric polarizations (see Table I). The electric polarization $\mathbf{P}$ is calculated to be along the *a*-direction for the *ab*-plane spin spiral, and along the $-c$-direction for the *bc*-plane spin spiral [31]. When the spin spiral is in the *ac*-plane, the electric polarization is calculated to be zero. The same results are also obtained for $LiCuVO_4$. Thus, for both $LiCu_2O_2$ and $LiCuVO_4$, the directions of the calculated electric polarizations are consistent with the prediction of the KNB model. This agreement is somewhat surprising since the KNB model was derived for a linear trimer M-O-M with t_{2g} transition metal ions M [7]. The calculated electric polarizations are anisotropic, e.g., the electric polarizations of $LiCu_2O_2$ are 51.4 and 9.8 $\mu C/m^2$ for the *ab*- and *bc*-plane spin spiral arrangements, respectively. Note that the anisotropy in electric polarizations is not predicted by the KNB model.

Our calculations of electric polarizations show that the observed spin-spiral plane is consistent with the observed direction of the electric polarization for $LiCuVO_4$, but this is not the case for $LiCu_2O_2$. It is of interest to consider a probable reason for the latter discrepancy. For $LiCuVO_4$ [25], the planes of their spin spiral can be flipped by the application of an external magnetic field. For $LiCu_2O_2$ [11], the direction of the electric polarization can be flipped by an external magnetic field. In the ideal crystal structure of $LiCu_2O_2$, the CuO_2 ribbon chains with Cu^{2+} ions are interconnected by linear O-Cu-O bridges with diamagnetic Cu^+ ions. Matsuda *et al.* reported that the actual composition of their "$LiCu_2O_2$" sample is given by $Li_{1.16}Cu_{1.84}O_{2.01}$, in which 16% Cu^{2+} sites of the CuO_2 ribbon chains are replaced with diamagnetic Li^+ ions due to a good match of the ionic radii of Li^+ and Cu^{2+} while 16% Cu^+ ions in the linear O-Cu-
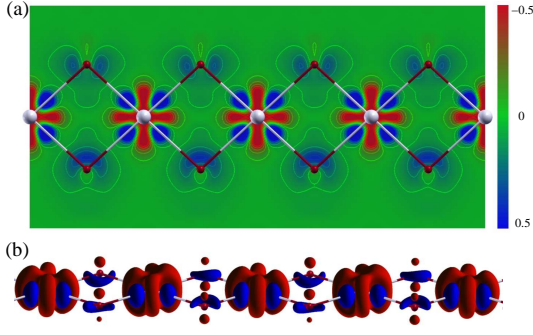
FIG. 3: (color online) (a) Cross section view of the electron density difference between the LDA+U+SOC and LDA+U calculations for the ab-plane spin spiral state (Fig. 2(a)) of LiCuVO$_4$. (b) Perspective view of an isosurface calculated for the electron density difference between the LDA+U+SOC and LDA+U results for the bc-plane spiral state (Fig. 2(c)) of LiCuVO$_4$. The red and blue surfaces represent -0.25 and 0.25, respectively.

FIG. 4: (color online) Difference in the PDOS plots of the adjacent Cu atoms, i.e., the Cu2 and Cu1 atoms of Fig. 2(a), in the (a) ab- and (b) bc-plane spin spiral state of LiCuVO$_4$. The energy region plotted corresponds to the hole xy state of LiCuVO$_4$.

O bridges become Cu^{2+} ions due to the charge balance requirement. This implies that the spins of the Cu^{2+} ions residing in between the CuO$_2$ ribbon chains can act as a source of "external" magnetic field for the CuO$_2$ ribbon chains, and hence can influence the plane of spin spiral in the CuO$_2$ ribbon chains. Similarly, the Ising behavior of CuFeO$_2$ with high spin Fe^{3+} (d^5) ions below 14 K has been explained in terms of a uniaxial magnetic field associated with oxygen defects [26]. Since the nonstoichiometry of "LiCu$_2$O$_2$" samples would depend strongly on synthetic conditions, it is highly desirable to measure the plane of spin spiral and the direction of electric polarization by using the same sample.

To test the conclusion of Jia et $al.$ [17] that the SOC on the O 2p orbitals is more important for the ferroelectric polarization of LiCuVO$_4$ than is the SOC on the Cu 3d orbitals, we carried out LDA+U+SOC calculations for LiCuVO$_4$ with the ab-plane spiral state by switching off the SOC on either the Cu or the O sites. When the SOC is neglected on the Cu sites but kept on the O sites, the electric polarization is calculated to be along the $-a$ axis with $P_a = -29.8$ $\mu C/m^2$. If the SOC is kept on the Cu sites but neglected on the O sites, the electric polarization is calculated to be along the a axis with $P_a = 127.1$ $\mu C/m^2$. The sum of the above two polarizations is very close to the electric polarization ($P_a = 103.5$ $\mu C/m^2$) calculated when the SOC is kept on both Cu and O sites. Therefore, the primary contribution to the electric polarization comes from the SOC on the Cu sites, which is greater than that from the SOC on the O sites by a factor of approximately four.

The dominance of the SOC on the Cu sites does not necessarily mean that the asymmetric charge distribution, needed for nonzero electric polarization, is associated mainly with the Cu atoms. To examine how the
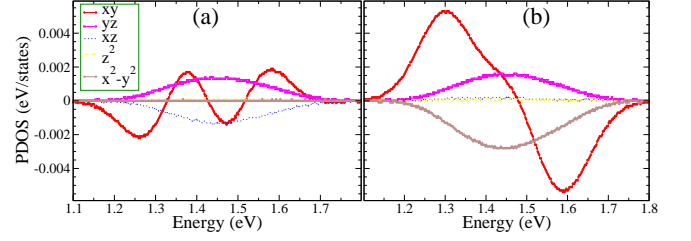
FE arises from the spiral magnetic state, we analyze the electron density distribution of the spin spiral state of LiCuVO$_4$ by plotting the difference between the electron density of the LDA+U+SOC calculation and that of the LDA+U calculation. For the case of the ab-plane spin spiral, Fig. 3(a) shows that the difference density around each Cu ion is almost symmetric, and hence contributes little to the electric polarization. However, an asymmetric difference density is found on the O atoms such that a nonzero electric polarization sets in along the a-direction. Fig. 3(b) shows a perspective view of the difference density plot for the case of the bc-plane spin spiral. Again, the difference density around each Cu atom is nearly symmetric, and an asymmetric difference density is found at each O atom largely along the c-direction eventually leading to the electric polarization along the c-direction.

From the viewpoint of local bonding, the SOC at each Cu site mixes into the hole xy state other 3d-states (i.e., the $x^2 - y^2$, xz, and yz states). The extent of the mixing for each 3d-state depends on the spin direction at a given Cu site because of the SOC term $\lambda S \cdot L$. This gives rise eventually to the asymmetric electron density distribution on the O sites because each 3d state of a given Cu site has the 2p orbitals of its surrounding O atoms combined out-of-phase with the Cu 3d orbital. We confirmed this point in two ways. First, we analyzed the partial density of states (PDOS) for the hole states of LiCuVO$_4$ (i.e., the unoccupied band associated with the down-spin xy state from each Cu site), which are located in the energy range from 1.1 to 1.8 eV above the Fermi level. In the spin spiral state, the neighboring Cu ions in each CuO$_2$ chain with different spin directions will have slightly different 3d PDOS because the mixing between the 3d-states induced by the SOC depends on the spin direction. As expected, the Cu1 and Cu2 ions [as defined in Fig. 2(a)] show differences in their PDOS not only for the ab-plane spin spiral (Fig. 4(a)) but also for the bc-plane spin spiral (Fig. 4(b)). Second, we extended the tight-binding calculations of Jia et $al.$ [8] to a tetramer model in which two Cu ions are bridged by two O ions as found in the CuO$_2$ ribbon chains, and carried out nu-

merical solutions by using all 3d orbitals of Cu and all 2p orbitals of O. As expected, the occupations of the $x^2 - y^2$, xz, and yz states at a given Cu site are found to depend on the spin direction of that site. In addition to a transverse electric dipole moment, a nonzero polarization is found along the Cu chain direction. This latter longitudinal component oscillates as the spin spiral progresses along the chain, and hence its effect is canceled out. Consequently, the overall polarization is calculated to be along the a and c directions in the case of the ab- and bc-plane spin spiral arrangements, respectively.

Concerning the effect of SOC on the FE in spiral magnets, there is a debate as to whether the FE arises from pure electronic effects [7, 17] or displacements of ions [9]. Using first principles calculations without taking SOC into account, Picozzi et $al.$ [27] showed that both factors are active for the FE in $HoMnO_3$. In our calculations described above, we used the experimental centrosymmetric structure for both $LiCu_2O_2$ [28] and $LiCuVO_4$ [29]. To evaluate the effect of polar atomic displacements on the electric polarization, we optimized the crystal structures by LDA+U+SOC calculations until the atomic forces become less than 0.01 eV/Å[32]. The calculated electric polarizations using the resulting relaxed structures are shown in Table I, which shows that the direction of the electric polarizations remains unchanged but the magnitude of the electric polarization becomes strongly enhanced by the structural relaxations. It is found that the Cu^{2+} ions move along the $-a$ and c directions in the case of the ab- (Fig. 2(a)) and bc-plane (Fig. 2(c)) spin spiral states, respectively. With respect to the centrosymmetric structure, however, the largest displacement of the Cu^{2+} ions is about 0.0004 Å, which are hardly detectable in experiment. Note that the experimental electric polarization at 2.5 K for $LiCu_2O_2$ is 4 $\mu C/m^2$, which is reasonably well reproduced by the calculation using the experimental structure (i.e., 9.8 $\mu C/m^2$). The electric polarization 191.8 $\mu C/m^2$ calculated by using the relaxed structure is much greater. Since the polar atomic displacements associated with the relaxation are extremely small, it is probable that their effects are negated by zero point vibrational effects.

To probe how one might improve the effect of multiferroicity, it is necessary to examine how SOC affects electric polarization. For this purpose, we performed LDA+U+SOC calculations for LiCuVO4 by treating the speed of light c as an adjustable parameter and noting that the strength of SOC is inversely proportional to the square of the speed of light c [30]. These hypothetical calculations show that the magnitude of electric polarization is proportional to the strength of SOC. Since the SOC of an atom increases in strength with increasing the atomic number, high-temperature multiferroics with large electric polarization are expected from spin-spiral systems with 4d or 5d transition metal elements. Another important factor is that the critical temperature of

the spin spiral ordering should be high.

In summary, our study of $LiCuVO_4$ and $LiCu_2O_2$ reveals that SOC is responsible for their FE, the primary contribution to the FE arises from the SOC on the Cu sites, but the asymmetric density distribution responsible for the electric polarization occurs mainly around the O atoms. For both $LiCuVO_4$ and $LiCu_2O_2$, the electric polarization is calculated to be much greater for the ab- than for the bc-plane spin spiral. The observed spin-spiral plane is consistent with the observed direction of the electric polarization for $LiCuVO_4$. However, this is not the case for $LiCu_2O_2$. To resolve the latter discrepancy, further experimental and theoretical studies are necessary.

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[24] The electric polarization can be understood as a sum of the contributions from individual CuO_2 chains. The sign of the contribution from each CuO_2 chain depends largely on its spin chirality. This supports the simulation of a spiral state with $\mathbf{q} = (0, 0.25, 0)$ instead of $\mathbf{q} = (0.5, 0.25, 0)$, which requires a $2\times4\times1$ supercell. Test calculations using $1 \times 6 \times 1$ supercell with the corresponding $\mathbf{q} = (0, 1/6, 0)$ give qualitatively similar results.

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[31] Our LDA+U+SOC calculations show spontaneous electric polarization in the spin spiral state even when the atom positions are kept to have the centrosymmetric space group. This is so because the mixing between electronic states induced by SOC leads to an electronic state that lacks inversion symmetry.

[32] In our structural optimizations, the P1 symmetry was used, i.e., no symmetry constraint was imposed. Obviously, inversion symmetry is lost after geometry optimization. Within the tolerance limit of 0.00002 Å, the space groups of the ab- and bc-plane spin spiral states of $LiCu_2O_2$ are Pc and P21, respectively, while those of the ab- and bc-plane spin spiral states of $LiCuVO_4$ are both P1.